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In re Patent Application of

Date: April 14, 2005

Applicants: Bednorz et al.

Docket: YO987-074BZ

Serial No.: 08/479,810

Group Art Unit: 1751

Filed: June 7, 1995

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

AFFIDAVIT UNDER 37 C.F.R. 1.132

Sir:

I, Thomas M. Shaw, being duly sworn, do hereby depose and state:

1. I received a B. S. degree in Metallurgy from the University of Liverpool, Liverpool, England and a M. S. and a Ph.D. degree in Material Science (1981) from the University of California, Berkeley.
2. I refer to Attachments A to Z and AA herein which were submitted in a separate paper designated as "FIRST SUPPLEMENTAL AMENDMENT" in response to the Office Action dated July 28, 2004. I also refer to Attachments AB to AG which were submitted in a separate paper designated as "THIRD SUPPLEMENTAL AMENDMENT" in response to the Office Action dated July 28, 2004.
3. I have worked as a postdoctoral researcher in the Material Science Department of Cornell University from 1981-1982. I have worked at Rockwell International Science Center in Thousand Oaks, California from 1982-1984 as a ceramic scientist. I have worked as a research staff member in Ceramics Science at the Thomas J. Watson Research Center of the International Business Machines Corporation in Yorktown Heights, New York from 1984 to the present.

4. I have worked in the fabrication of and characterization of ceramic materials of various types, including superconductors and related materials from 1984 to the present.
5. My resume and list of publications is in Attachment 1 included with this affidavit.
6. This affidavit is in addition to my affidavit dated December 15, 1998. I have reviewed the above-identified patent application (Bednorz-Mueller application) and acknowledge that it represents the work of Bednorz and Mueller, which is generally recognized as the first discovery of superconductivity in a material having a $T_c \geq 26^\circ\text{K}$ and that subsequent developments in this field have been based on this work.
7. All the high temperature superconductors which have been developed based on the work of Bednorz and Mueller behave in a similar manner, conduct current in a similar manner, have similar magnetic properties, and have similar structural properties.
8. Once a person of skill in the art knows of a specific type of composition described in the Bednorz-Mueller application which is superconducting at greater than or equal to 26°K , such a person of skill in the art, using the techniques described in the Bednorz-Mueller application, which includes all principles of ceramic fabrication known at the time the application was initially filed, can make the compositions encompassed by the claims of the Bednorz-Mueller application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art of the fabrication of ceramic materials. This is why the work of Bednorz and Mueller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period after their discovery. Bednorz and Mueller's discovery was first reported in Z. Phys. B 64 page 189-193 (1996).
9. The techniques for placing a superconductive composition into a superconducting state have been known since the discovery of superconductivity in 1911 by Kamerlingh-Onnes.

10. Prior to 1986 a person having a bachelor's degree in an engineering discipline, applied science, chemistry, physics or a related discipline could have been trained within one year to reliably test a material for the presence of superconductivity and to flow a superconductive current in a superconductive composition.

11. Prior to 1986 a person of ordinary skill in the art of fabricating a composition according to the teaching of the Bednorz-Mueller application would have: a) a Ph.D. degree in solid state chemistry, applied physics, material science, metallurgy, physics or a related discipline and have done thesis research including work in the fabrication of ceramic materials; or b) have a Ph.D. degree in these same fields having done experimental thesis research plus one to two years post Ph.D. work in the fabrication of ceramic materials; or c) have a master's degree in these same fields and have had five years of materials experience at least some of which is in the fabrication of ceramic materials. Such a person is referred to herein as a person of ordinary skill in the ceramic fabrication art.

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12. The general principles of ceramic science referred to by Bednorz and Mueller in their patent application and known to a person of ordinary skill in the ceramic fabrication art can be found in many books and articles published before their discovery, priority date (date of filing of their European Patent Office patent application EPO 0275343A1, January 23, 1987) and initial US Application filing date (May 22, 1987). An exemplary list of books describing the general principles of ceramic fabrication are:

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a) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is in Attachment B.

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b) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is in Attachment C.

- c) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is in Attachment D.
- d) Structure, Properties and Preparation of Perovskite-Type Compounds, F. S. Galasso, Pergamon Press, 1969, in particular pages 159-186, a copy of which is in Attachment E.

These references were previously submitted with the Affidavit of Thomas Shaw submitted December 15, 1998.

13. An exemplary list of articles applying the general principles of ceramic fabrication to the types of materials described in Applicants' specification are:

- a) Oxygen Defect K_2NiF_4 - Type Oxides: The Compounds $La_{2-x}Sr_xCuO_{4-x/2+}$, Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981). See Attachment F.
- b) The Oxygen Defect Perovskite $BaLa_4Cu_5O_{13.4}$, A Metallic (This is referred to in the Bednorz-Mueller application at page 21, lines 1-2) Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985. See Attachment G.
- c) Oxygen Intercalation in Mixed Valence Copper Oxides Related to the Perovskite, C. Michel et al., Revue de Chemie Minerale, 21, p. 407, 1984. (This is referred to in the Bednorz-Mueller application at page 27, lines 1-2). See Attachment H.
- d) Thermal Behaviour of Compositions in the Systems $x BaTiO_3 + (1-x) Ba(Ln_{0.5}B_{0.5})O_3$, V.S. Chincholkar et al., Therm. Anal. 6th, Vol. 2., p. 251-6, 1980. See Attachment I.

14. The Bednorz-Mueller application in the paragraph bridging pages 6 and 7 states in regard to the high T_c materials:

These compositions can carry supercurrents (i.e., electrical currents in a substantially zero resistance state of the composition) at temperatures greater than 26°K. In general, the compositions are characterized as mixed transition metal oxide systems where the transition metal oxide can exhibit multivalent behavior. These compositions have a layer-type crystalline structure, often perovskite-like, and can contain a rare earth or rare earth-like element. A rare earth-like element (sometimes termed a near rare earth element is one whose properties make it essentially a rare earth element. An example is a group IIIB element of the periodic table, such as La. Substitutions can be found in the rare earth (or rare earth-like) site or in the transition metal sites of the compositions. For example, the rare earth site can also include alkaline earth elements selected from group IIA of the periodic table, or a combination of rare earth or rare earth-like elements and alkaline earth elements. Examples of suitable alkaline earths include Ca, Sr, and Ba. The transition metal site can include a transition metal exhibiting mixed valent behavior, and can include more than one transition metal. A particularly good example of a suitable transition metal is copper. As will be apparent later, Cu-oxide based systems provide unique and excellent properties as high T_c superconductors. An example of a superconductive composition having high T_c is the composition represented by the formula RE-TM-O, where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen. Examples of transition metal elements include Cu, Ni, Cr etc. In particular, transition metals that can exhibit multi-valent states are very suitable. The rare earth elements are typically elements 58-71 of the periodic table, including Ce, Nd, etc.

15. In the passage quoted in paragraph 14 the general formula is RE-TM-O "where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen." This paragraph states "Substitutions can be found in the rare earth (or rare earth-like) site or in the transition metal sites of the compositions. For example, the rare earth site can also include alkaline earth elements selected from group IIA of the periodic table, or a combination of rare earth or rare earth-like elements and alkaline earth elements." Thus applicants teach that RE can be something other than an rare earth. For example, it can be an alkaline earth, but is not limited to a alkaline earth element. It can be an element that has the same effect as an alkaline earth or rare-earth element, that is a rare earth like element. Also, this passage teaches that TM can be substituted with another element, for example, but not limited to, a rare earth, alkaline earth or some other element that acts in place of the transition metal.

16. The following table is compiled from the Table 1 of the Article by Rao (See Attachment AB) and the Table of high T_c materials from the "CRC Handbook of Chemistry and Physics" 2000-2001 Edition (See Attachment AC). An asterisk in column 5 indicated that the composition of column 2 does not come within the scope of the claims allowed in the Office Action of July 28, 2004.

17. I have reviewed the Office Action dated July 28, 2004, which states at page 6 "The present specification is deemed to be enabled only for compositions comprising a transition metal oxide containing at least a) an alkaline earth element and b) a rare-earth element of Group IIIB element." I disagree for the reasons given herein.

18. Composite Table

1	2	3	4	5	6	7
#	MATERIAL	RAO ARTICLE	HANDBOOK OF CHEM & PHYSICS		ALKALINE EARTH ELEMENT	RARE EARTH ELEMENT
1	$\text{La}_2\text{CuO}_{4+\delta}$	√	√	*	N	Y
2	$\text{La}_{2-x}\text{Sr}_x(\text{Ba}_x)\text{CuO}_4$	√	√		Y	Y
3	$\text{La}_2\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_2\text{O}_6$	√	√		Y	Y

4	$\text{YBa}_2\text{Cu}_3\text{O}_7$	√	√		Y	Y
5	$\text{YBa}_2\text{Cu}_4\text{O}_8$	√	√		Y	Y
6	$\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$	√	√		Y	Y
7	$\text{Bi}_2\text{Sr}_2\text{CuO}_6$	√	√	*	Y	N
8	$\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	√	√	*	Y	N
9	$\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$	√	√	*	Y	N
10	$\text{Bi}_2\text{Sr}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10}$	√	√		Y	Y
11	$\text{Tl}_2\text{Ba}_2\text{CuO}_6$	√	√	*	Y	N
12	$\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$	√	√	*	Y	N
13	$\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$	√	√	*	Y	N
14	$\text{Tl}(\text{BaLa})\text{CuO}_5$	√	√		Y	Y
15	$\text{Tl}(\text{SrLa})\text{CuO}_5$	√	√		Y	Y
16	$(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{CuO}_5$	√	√	*	Y	N
17	$\text{TlCaBa}_2\text{Cu}_2\text{O}_7$	√	√	*	Y	N
18	$(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{CaSr}_2\text{Cu}_2\text{O}_7$	√	√	*	Y	N
19	$\text{TlSr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_7$	√	√		Y	Y
20	$\text{TlCa}_2\text{Ba}_2\text{Cu}_3\text{O}_8$	√	√	*	Y	N
21	$(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$	√	√	*	Y	N
22	$\text{TlBa}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_9$	√	√		Y	Y
23	$\text{Pb}_2\text{Sr}_2\text{Ln}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$	√	√		Y	Y
24	$\text{Pb}_2(\text{Sr}_x\text{La})_2\text{Cu}_2\text{O}_6$	√	√		Y	Y
25	$(\text{Pb,Cu})\text{Sr}_2(\text{Ln,Ca})\text{Cu}_2\text{O}_7$	√	√		Y	Y
26	$(\text{Pb,Cu})(\text{Sr,Eu})(\text{Eu,Ce})\text{Cu}_2\text{O}_x$	√	√		Y	Y
27	$\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$	√	√	*	N	Y
28	$\text{Ca}_{1-x}\text{Nd}_x\text{CuO}_2$	√			Y	Y
29	$\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$	√	√		Y	Y
30	$\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$		√	*	Y	N
31	$\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$		√	*	Y	N
32	$\text{Rb}_2\text{C}_5\text{C}_{60}$		√	*	N	Y
33	$\text{NdBa}_2\text{Cu}_3\text{O}_7$		√		Y	Y
34	SmBaSrCuO_7		√		Y	Y
35	$\text{EuBaSrCu}_3\text{O}_7$		√		Y	Y
36	$\text{BaSrCu}_3\text{O}_7$		√	*	Y	N
37	$\text{DyBaSrCu}_3\text{O}_7$		√		Y	Y
38	$\text{HuBaSrCu}_3\text{O}_7$		√		Y	Y
39	$\text{ErBaSrCu}_3\text{O}_7$ (Multiphase)		√		Y	Y
40	$\text{TmBaSrCu}_3\text{O}_7$ (Multiphase)		√		Y	Y

41	YBaSrCu ₃ O ₇		√	*	Y	Y
42	HgBa ₂ CuO ₂		√	*	Y	N
43	HgBa ₂ CaCu ₂ O ₆ (annealed in O ₂)		√	*	Y	N
44	HgBa ₂ Ca ₂ Cu ₃ O ₈		√	*	Y	N
45	HgBa ₂ Ca ₃ Cu ₄ O ₁₀		√	*	Y	N

19. The first composition, La₂ Cu O_{4+δ}, has the form RE₂CuO₄ which is explicitly taught by Bednorz and Mueller. The δ indicates that there is a nonstoichiometric amount of oxygen.

20. The Bednorz-Mueller application teaches at page 11, line 19 to page 12, line 7:

An example of a superconductive compound having a layer-type structure in accordance with the present invention is an oxide of the general composition RE₂TMO₄ where RE stands for the rare earths (lanthanides) or rare earth-like elements and TM stands for a transition metal. In these compounds the RE portion can be partially substituted by one or more members of the alkaline earth group of elements. In these particular compounds, the oxygen content is at a deficit. For example, one such compound that meets this general description is lanthanum copper oxide La₂CuO₄...

21. The Bednorz-Mueller application at page 15, last paragraph states "Despite their metallic character, the Ba-La-Cu-O type materials are essentially ceramics, as are other compounds of the RE₂ TMO₄ type, and their manufacture generally follows known principles of ceramic fabrication."

22. Compound number 27 of the composite table contains Nd and Ce, both rare earth elements. All of the other compounds of the composite table, except for number 32, have O and one of the alkaline earth elements which as stated above is explicitly taught by applicants. Compound 31 is a BiO_3 compound in which TM is substituted by another element, here Bi, as explicitly taught by Applicants in the paragraph quoted above.

23. The rare earth elements are Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. See the Handbook of Chemistry and Physics 59th edition 1978-1979 page B262 in Appendix A. The transition elements are identified in the periodic table from the inside front cover of the Handbook of Chemistry and Physics in Appendix A.

24. The basic theory of superconductivity has been known many years before Applicants' discovery. For example, see the book "Theory of Superconductivity", M. von Laue, Academic Press, Inc., 1952 (See Attachment AD).

25. In the composite table, compound numbers 7 to 10 and 31 are Bismuth (Bi) compounds. Compound number 12 to 22 are Thallium (Tl) compounds. Compound numbers 23 to 26 are lead (Pb) compounds. Compounds 42 to 45 are Mercury (Hg) compounds. Those compounds that do not come within the scope of an allowed claims (the compounds which are not marked with an asterisk in column 3 of the composite table) are primarily the Bi, Tl, Pb and Hg compounds. These compounds are made according to the principles of ceramic science known prior to applicant's filing date. For example, Attachments J, K, L, and M contain the following articles:

Attachment J - Phys. Rev. B. Vol. 38, No. 16, p. 6531 (1988) is directed to Thallium compounds.

Attachment K - Jap. Joun. of Appl. Phys., Vol. 27, No. 2, p. L209-L210 (1988) is directed to Bismuth (Bi) compounds.

Attachment L - Letter to Nature, Vol. 38, No. 2, p. 226 (18 March 1993) is directed to Mercury (Hg) compounds.

Attachment M - Nature, Vol. 336, p. 211 (17 November 1988) is directed to Lead (Pb) based compounds.

26. The article of Attachment J (directed to Tl compounds) states at page 6531, left column:

The samples were prepared by thoroughly mixing suitable amounts of Tl_2O_3 , CaO, BaO_2 , and CuO, and forming a pellet of this mixture under pressure. The pellet was then wrapped in gold foil, sealed in quartz tube containing slightly less than 1 atm of oxygen, and baked for approximately 3 h at $\approx 880^\circ C$.

This is according to the general principles of ceramic science known prior to applicant's priority date.

27. The article of Attachment K (directed to Bi compounds) states at page L209:

The Bi-Sr-Ca-Cu-O oxide samples were prepared from powder reagents of Bi_2O_3 , $SrCO_3$, $CaCO_3$ and CuO. The appropriate amounts of powders were mixed, calcined at $800-870^\circ C$ for 5 h, thoroughly reground and then cold-pressed into disk-shape pellets (20 mm in diameter and 2 mm in thickness) at a pressure of 2 ton.cm². Most of the pellets were sintered at about $870^\circ C$ in air or in an oxygen atmosphere and then furnace-cooled to room temperature.

This is according to the general principles of ceramic science known prior to applicant's priority date.

28. The article of Attachment L (directed to Hg compounds) states at page 226:

The samples were prepared by solid state reaction between stoichiometric mixtures of $\text{Ba}_2\text{CuO}_{3.6}$ and yellow HgO (98% purity, Aldrich). The precursor $\text{Ba}_2\text{CuO}_{3.6}$ was obtained by the same type of reaction between BaO_2 (95% purity, Aldrich) and CuO (NormalPur, Prolabo) at 930°C in oxygen, according to the procedure described by De Leeuw et al.⁶. The powders were ground in an agate mortar and placed in silica tubes. All these operations were carried out in a dry box. After evacuation, the tubes were sealed, placed in steel containers, as described in ref. 3, and heated for 5 h to reach $\sim 800^\circ\text{C}$. The samples were then cooled in the furnace, reaching room temperature after ~ 10 h.

This is according to the general principles of ceramic science known prior to applicant's priority date.

29. The article of Attachment M (directed to Pb compounds) states at page 211, left column:

The preparative conditions for the new materials are considerably more stringent than for the previously known copper-based superconductors. Direct synthesis of members of this family by reaction of the component metal oxides or carbonates in air or oxygen at temperatures below 900°C is not possible because of the stability of the oxidized SrPbO_3 -based perovskite. Successful synthesis is accomplished by the reaction of PbO with pre-reacted (Sr, Ca, Ln) oxide precursors. The precursors are prepared from oxides and carbonates in the appropriate metal ratios, calcined for 16 hours (in dense Al_2O_3 crucibles) at 920 - 980°C in air with one intermediate grinding.

This is according to the principles of ceramic science known prior to applicant's priority date.

30. A person of ordinary skill in the art of the fabrication of ceramic materials would be motivated by the teaching of the Bednorz-Mueller application to investigate compositions for high superconductivity other than the compositions specifically fabricated by Bednorz and Mueller.

31. In Attachment U, there is a list of perovskite materials from pages 191 to 207 in the book "Structure, Properties and Preparation of Perovskite-Type Compounds" by F. S. Galasso, published in 1969, which is Attachment E hereto. This list contains about 300 compounds. Thus, what the term "Perovskite-type" means and how to make these compounds was well known to a person of ordinary skill in the art in 1969, more than 17 years before the Applicants' priority date (January 23, 1987).

This is clear evidence that a person of skill in the art of fabrication of ceramic materials knows (prior to Applicants' priority date) how to make the types of materials in Table 1 of the Rao Article and the Table from the Handbook of Chemistry and Physics as listed in the composite table above in paragraph 17.

32. The standard reference "Landolt-Börnstein", Volumn 4, "Magnetic and Other Properties of Oxides and Related Compounds Part A" (1970) lists at page 148 to 206 Perovskite and Perovskite-related structures. (See Attachment N). Section 3.2 starting at page 190 is entitled "Descriptions of perovskite-related structures". The German title is "Perowskit-ähnliche Strukturen". The German word "ähnliche" can be translated in English as "like". The Langenscheidt's German-English, English-German Dictionary 1970, at page 446 translates the English "like" as the German "ähnliche". (See Attachment O). Pages 126 to 147 of Attachment N describes "crystallographic and magnetic properties of perovskite and perovskite-related compounds", see title of Section 3 at page 126. Section 3.2.3.1 starting at page 192 of "Landolt-Börnstein" Vol. 4 (See Attachment N) is entitled "Bismuth Compounds". Thus Bismuth

perovskite-like compounds and how to make them were well known more than 16 years prior to Applicants' priority date. Thus the "Landholt Börnstein" book published in 1970, more than 16 years before Applicants' priority date (January 23, 1987), shows that the term "perovskite-like" or "perovskite related" is understood by persons of skill in the art prior to Applicants' priority date. Moreover, the "Landholt-Börnstein" book cites references for each compound listed. Thus a person of ordinary skill in the art of ceramic fabrication knows how to make each of these compounds. Pages 376-380 of Attachment N has figures showing the crystal structure of compounds containing Bi and Pb.

33. The standard reference "Landholt-Börnstein, Volume 3, Ferro- and Antiferroelectric Substances" (1969) provides at pages 571-584 an index to substances. (See Attachment P). This list contains numerous Bi and Pb containing compounds. See, for example pages 578 and 582-584. Thus a person of ordinary skill in the art of ceramic fabrication would be motivated by Applicants' application to fabricate Bi and/or Pb containing compounds that come within the scope of the Applicants' claims.

34. The standard reference "Landholt-Börnstein Volume 3 Ferro- and Antiferroelectric Substances" (1969) (See Attachment P) at page 37, section 1 is entitled "Perovskite-type oxides." This standard reference was published more than 17 years before Applicants' priority date (January 23, 1987). The properties of perovskite-type oxides are listed from pages 37 to 88. Thus the term perovskite-type was well known and understood by persons of skill in the art of ceramic fabrication prior to Applicants' priority date and more than 17 years before Applicants' priority date persons of ordinary skill in the art knew how to make Bi, Pb and many other perovskite, perovskite-like, perovskite-related and perovskite-type compounds.

35. At page 14, line 10-15 of the Bednorz-Mueller application, Applicants' state "samples in the Ba-La-Cu-O system, when subjected to x-ray analysis, revealed three individual crystallographic phases V.12. a first layer-type perovskite-like phase, related to the K_2NiF_4 structure ..." Applicants' priority document EP0275343A1 filed July 27, 1988, is entitled "New Superconductive Compounds of the K_2NiF_4 Structural Type Having a High Transition Temperature, and Method for Fabricating Same." See (See Attachment AE). The book "Structure and Properties of Inorganic Solids" by Francis S. Galasso, Pergamon Press (1969) at page 190 lists examples of Thallium (Tl) compounds in the K_2NiF_4 structure. (See Attachment Q). Thus based on Applicants' teachings prior to Applicants' priority date, a person of ordinary skill in the art of ceramic fabrication would be motivated to fabricate Thallium based compounds to test for high T_c superconductivity.

36. The book "Crystal Structures" Volume 4, by Ralph W. G. Wyckoff, Interscience Publishers, 1960 states at page 96 "This structure, like these of $Bi_4Ti_2O_{12}$ (IX, F_{12}) and $BaBi_4Ti_4O_4$ (XI, 13) is built up of alternating Bi_2O_2 and perovskite-like layers." Thus layer of perovskite-like Bismuth compounds was well known in the art in 1960 more than 26 years before Applicants' priority date. (See Attachment R).

37. The book "Modern Oxide Materials Preparation, Properties and Device Applications" edited by Cockayne and Jones, Academic Press (1972) states (See Attachment S) at page 155 under the heading "Layer Structure Oxides and Complex Compounds":

"A large number of layer structure compounds of general formula $(Bi_2O_2)^{2+}(A_{x-1}B_xO_{3x+1})^{2-}$ have been reported (Smolenskii et al. 1961; Subbarao, 1962), where A = Ca, Sr, Ba, Pb, etc., B = Ti, Nb, Ta and x = 2, 3, 4, or 5. The structure had been previously investigated by Aurivillius (1949) who described them in terms of Alternate $(Bi_2O_2)^{2+}$ layers and perovskite layers of oxygen octahedra. Few have been found to be ferroelectric and include $SrBi_2Ta_2O_9$ ($T_c = 583^\circ K$), $PbBi_2Ta_2O_9$ ($T_c = 703^\circ K$), $BiBi_3Ti_2TiO_{12}$ or

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($T_c = 948^\circ\text{K}$), $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ($T_c = 598^\circ\text{K}$) and $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ($T_c = 583^\circ\text{K}$). Only bismuth titanate $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has been investigated in detail in the single crystal form and is finding applications in optical stores (Cummins, 1967) because of its unique ferroelectric-optical switching properties. The ceramics of other members have some interest because of their dielectric properties. More complex compounds and solid solutions are realizable in these layer structure oxides but none have significant practical application."

Thus the term layered oxides was well known and understood prior to Applicants' priority date. Moreover, layered Bi and Pb compounds were well known in 1972 more than 15 years before Applicants' priority date.

38. The standard reference "Landolt-Börnstein, Volume 3, Ferro and Antiferroelectric Substances" (1969) at pages 107 to 114 (See Attachment T) list "layer-structure oxides" and their properties. Thus the term "layered compounds" was well known in the art of ceramic fabrication in 1969 more than 16 years prior to Applicants' priority date and how to make layered compounds was well known prior to applicants priority date.

39. Layer perovskite type Bi and Pb compounds closely related to the Bi and Pb high T_c compounds in the composite table above in paragraph 17 have been known for some time. For example, the following is a list of four articles which were published about 35 years prior to Applicants' first publication date:

(1) Attachment V - "Mixed bismuth oxides with layer lattices", B. Aurivillius, Arkiv Kemi 1, 463, (1950).

(2) Attachment W - "Mixed bismuth oxides with layered lattices", B. Aurivillius, Arkiv Kemi 1, 499, (1950).

(3) Attachment X - "Mixed bismuth oxides with layered lattices ", B. Aurivillius, Arkiv Kemi 2, 519, (1951).

(4) Attachment Y - "The structure of $\text{Bi}_2\text{NbO}_5\text{F}$ and isomorphous compounds", B. Aurivillius, Arkiv Kemi 5, 39, (1952).

These articles will be referred to as Aurivillius 1, 2, 3 and 4, respectively.

40. Attachment V (Aurivillius 1), at page 463, the first page, has the subtitle "I. The structure type of $\text{CaNb}_2\text{Bi}_2\text{O}_9$. Attachment V states at page 463:

X-ray analysis ... seemed to show that the structure was built up of Bi_2O_2^+ layers parallel to the basal plane and sheets of composition $\text{Bi}_2\text{Ti}_3\text{O}_{10}^-$. The atomic arrangement within the $\text{Bi}_2\text{Ti}_3\text{O}_{10}^-$ sheets seemed to be the same as in structure of the perovskite type and the structure could then be described as consisting of Bi_2O_2^+ layers between which double perovskite layers are inserted.

41. Attachment V (Aurivillius 1) at page 464 has a section entitled " $\text{PbBi}_2\text{Nb}_2\text{O}_9$ Phase". And at page 471 has a section entitled " $\text{Bi}_3\text{NbTiO}_9$ ". And at page 475 has a table of compounds having the " $\text{CaBi}_2\text{Nb}_2\text{O}_9$ structure" listing the following compounds $\text{Bi}_3\text{NbTiO}_9$, $\text{Bi}_3\text{TaTiO}_9$, $\text{CaBi}_2\text{Nb}_2\text{O}_9$, $\text{SrBi}_2\text{Nb}_2\text{O}_9$, $\text{SrBi}_2\text{Ta}_2\text{O}_9$, $\text{BaBi}_2\text{Nb}_2\text{O}_9$, $\text{PbBi}_2\text{Nb}_2\text{O}_9$, $\text{NaBi}_5\text{Nb}_4\text{O}_{18}$, $\text{KBi}_5\text{Nb}_4\text{O}_{18}$. Thus Bi and Pb layered perovskite compounds were well known in the art about 35 years prior to Applicants' priority date.

42. Attachment W (Aurivillius 2) at page 499, the first page, has the subtitle "II Structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ". And at page 510, Fig. 4 shows a crystal structure in which "A denotes a perovskite layer $\text{Bi}_2\text{Ti}_3\text{O}_{10}^-$, C Bi_2O_2^+ layers and B unit cells of the hypothetical perovskite structure BiTiO_3 .

43. Attachment X (Aurivillius 3) has at page 519, the first page, the subtitle "III Structure of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ". And in the first paragraph on page 519 states referring to the articles of Attachments V (Aurivillius 1), and W (Aurivillius 2) "X ray studies on the compounds $\text{CaBi}_2\text{Nb}_2\text{O}_9$ [the article of Attachment V] and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [the article of Attachment W] have shown that the comparatively complicated chemical formulae of these compounds can be explained by simple layer structures being built up from Bi_2O_2^+ layers and perovskite layers. The unit cells are pictured schematically in Figs. 1a and 1c." And Fig. 4 at page 526 shows "One half of a unit cell of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$. A denotes the perovskite region and B the Me_2O_4 layer" where Me represents a metal atom.

44. Attachment Y (Aurivillius 4) is direct to structures having the $\text{Bi}_3\text{N}_{10}\text{O}_3\text{F}$ structure.

45. Attachment AA is a list of Hg containing solid state compounds from the 1989 Powder Diffraction File Index. Applicants do not have available to them an index from prior to Applicants' priority date. The Powder Diffraction File list is a compilation of all known solid state compounds with reference to articles directed to the properties of these compositions and the methods of fabrication. From Attachment AA it can be seen, for example, that there are numerous examples of Hg based compounds. Similarly, there are examples of other compounds in the Powder Diffraction File. A person of ordinary skill in the art is aware of the Powder Diffraction File and can from this file find a reference providing details on how to fabricate these compounds. Thus persons of ordinary skill in the art would be motivated by Applicants' teaching to look to the Powder Diffraction File for examples of previously fabricated composition expected to have properties similar to those described in Applicants' teaching.

46. It is generally recognized that it is not difficult to fabricate transition metal oxides and in particular copper metal oxides that are superconductive after the discovery by Applicants of composition, such as transition metal oxides, that are high T_c superconductors. This is noted in the book "Copper Oxide Superconductors" by Charles P. Poole, Jr., Timir Datta and Horacio A. Farach, John Wiley & Sons (1998),

referred to herein as Poole 1988: Chapter 5 of Poole 1988 (See Attachment AF) in the book entitled "Preparation and Characterization of Samples" states at page 59 "[c]opper oxide superconductors with a purity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials". Poole 1988 further states at page 61 "[i]n this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol-gel techniques (Hatfi). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors, and it requires little familiarity with the subtle physicochemical process involved in the transformation of a mixture of compounds into a superconductor." Poole 1988 further states at pages 61-62 "[i]n the solid state reaction technique one starts with oxygen-rich compounds of the desired components such as oxides, nitrates or carbonates of Ba, Bi, La, Sr, Ti, Y or other elements. ... These compounds are mixed in the desired atomic ratios and ground to a fine powder to facilitate the calcination process. Then these room-temperature-stable salts are reacted by calcination for an extended period (~20hr) at elevated temperatures (~900°C). This process may be repeated several times, with pulverizing and mixing of the partially calcined material at each step." This is generally the same as the specific examples provided by Applicants and as generally described at pages 8, line 19, to page 9, line 5, of the Bednorz-Mueller application which states "[t]he methods by which these superconductive compositions can be made can use known principals of ceramic fabrication, including the mixing of powders containing the rare earth or rare earth-like, alkaline earth, and transition metal elements, coprecipitation of these materials, and heating steps in oxygen or air. A particularly suitable superconducting material in accordance with this invention is one containing copper as the transition metal." Consequently, it is my opinion that Applicants have fully enabled high T_c materials oxides and their claims.

47. Charles Poole et al. published another book in 1995 entitled "Superconductivity" Academic Press which has a Chapter 7 on "Perovskite and Cuprate Crystallographic Structures". (See Attachment Z). This book will be referred to as Poole 1995.

At page 179 of Poole 1995 states:

V. PEROVSKITE-TYPE SUPERCONDUCTING STRUCTURES

In their first report on high-temperature superconductors Bednorz and Müller (1986) referred to their samples as "metallic, oxygen-deficient ... perovskite-like mixed-valence copper compounds." Subsequent work has confirmed that the new superconductors do indeed possess these characteristics.

I agree with this statement.

48. The book "The New Superconductors", by Frank J. Owens and Charles P. Poole, Plenum Press, 1996, referred to herein as Poole 1996 in Chapter 8 entitled "New High Temperature Superconductors" starting a page 97 (See Attachment AG) shows in Section 8.3 starting at page 98 entitled "Layered Structure of the Cuprates" schematic diagrams of the layered structure of the cuprate superconductors. Poole 1996 states in the first sentence of Section 8.3 at page 98 "All cuprate superconductors have the layered structure shown in Fig. 8.1." This is consistent with the teaching of Bednorz and Mueller that "These compositions have a layer-type Crystalline Structure often Perovskite-like" as noted in paragraph 14 above. Poole 1996 further states in the first sentence of Section 8.3 at page 98 "The flow of supercurrent takes place in conduction layers and bonding layers support and hold together the conduction layers". The caption of Fig. 8.1 states "Layering scheme of the cuprate superconductors". Fig. 8.3 shows details of the conduction layers for difference sequence of copper oxide planes and Fig. 8.4 presents details of the bonding layers for several of the cuprates which include binding layers for lanthanum superconductor La_2CuO_4 , neodymium superconductor Nd_2CuO_4 , yttrium superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{2n+4}$, bismuth

superconductor $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$, thallium superconductor $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$, and mercury superconductor $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$. Fig. 8.5 at pages 102 and 103 show a schematic atomic structure showing the layering scheme for thallium superconductors. Fig. 8.10 at page 109 shows a schematic crystal structure showing the layering scheme for La_2CuO_4 . Fig. 8.11 at page 110 shows a schematic crystal structure showing the layering scheme for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$. The layering shown in Poole 1996 for high T_c superconductors is consistent with the layering as taught by Bednorz and Mueller in their patent application.

49. Thus Poole 1988 states that the high T_c superconducting materials "are not difficult to synthesize" and Poole 1995 states that "the new superconductors do indeed possess [the] characteristics" that Applicants' specification describes these new superconductors to have. Poole 1996 provide details showing that high T_c superconductors are layered or layer-like as taught by Bednorz and Mueller. Therefore, as of Applicants' priority date persons of ordinary skill in the art of ceramic fabrication were enabled to practice Applicants' invention to the full scope that it is presently claimed, including in the claims that are not allowed from the teaching in the Bednorz-Mueller application without undue experimentation that is by following the teaching of Bednorz and Mueller in combination with what was known to persons of ordinary skill in the art of ceramic fabrication. The experiments to make high T_c superconductors not specifically identified in the Bednorz-Mueller application were made by principles of ceramic fabrication prior to the date of their first publication. It is within the skill of a person of ordinary skill in the art of ceramic fabrication to make compositions according to the teaching of the Bednorz-Mueller application to determine whether or not they are high T_c superconductors without undue experimentation.

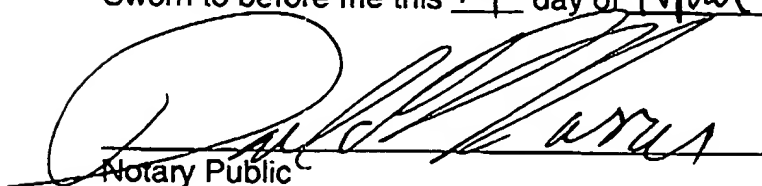
50. I have personally made many samples of high T_c superconductors following the teaching of Bednorz and Mueller as found in their patent applications. In making these materials it was not necessary to use starting materials in stoichiometric proportions to produce a high T_c superconductor with insignificant secondary phases or multi-phase compositions, having a superconducting portion and a non-superconducting portion, where the composite was a high T_c superconductor. Consequently, following the teaching of Bednorz and Mueller and principles of ceramic science known prior to their discovery, I made, and persons of skill in the ceramic arts were able to make, high T_c superconductors without exerting extreme care in preparing the composition. Thus I made and persons of skill in the ceramic arts were able to make high T_c superconductors following the teaching of Bednorz and Mueller, without experimentation beyond what was well known to a person of ordinary skill in the ceramic arts prior to the discovery by Bednorz and Mueller.

51. I hereby swear that all statements made herein of my knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements made jeopardize the validity of the application or patent issued thereon.

Date: 14th April 2005

By: Thomas M. Shaw
Thomas M. Shaw

Sworn to before me this 14 day of April, 2005.


Notary Public

DANIEL P. MORRIS
NOTARY PUBLIC, State of New York
No. 4888676
Qualified in Westchester County
Commission Expires March 16, 192007

ATTACHMENT 1

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Education:

1981 Ph.D.	Materials Science - University of California at Berkeley
1978 Masters of Science	Materials Science - University of California at Berkeley
1975 Bachelors of Science	Engineering in Metallurgy and Materials Science - University of Liverpool

Work Experience:

1994-Present Research Staff Member at IBM Thomas J. Watson Research Center working in Materials Science
1984-1994 Research Staff Member at IBM Thomas J. Watson Research Center working in Ceramics Science
1982-1984 Member of the technical staff at Rockwell International Science Center working in Ceramics Science
1981-1982 Postdoctoral Associate at Cornell University working in Ceramics Science

Professional Positions:

A fellow of the American Ceramics Society

Honors:

1981 John E. Dorn Award for thesis.

Publications:

Has authored or co-authored more that 150 publications and 21 patents.

His research interests include, ferroelectric thin films, processing and microstructure control of ceramic materials, microscopy of materials, interfacial energy driven processes, liquid phase sintering, porous materials, diffusion in thin films, electrical and mechanical properties materials and the reliability of interconnect structures.